

FR 1,274,732

---

Job No.: 1505-88034

Translated from French by the Ralph McElroy Translation Company  
910 West Avenue, Austin, Texas 78701 USA

FRENCH REPUBLIC  
MINISTRY OF INDUSTRY  
DEPARTMENT OF INDUSTRIAL PROPERTY  
FRENCH PATENT NO. 1,274,732

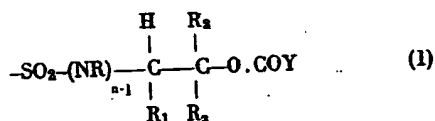
Int. Cl.:	C 09 b
Filing No.:	841.006
Filing Date:	October 12, 1960, 4:30 p.m., Paris
Date Granted:	September 18, 1961
[Published:]	Bulletin officiel de la Propriété industrielle, No. 43, 1961
[Priority:]	2 patent applications filed in the United Kingdom, October 12, 1959 and September 21, 1960, under the No. 34.480/1959 in the name of the applicant

NEW WATER-SOLUBLE COLORING SULFONES

Applicant:	Company known as: Imperial Chemical Industries Limited, residing in the United Kingdom
------------	--

The present invention relates to new coloring agents. More particularly, the invention relates to coloring agents which are water-soluble and capable of reacting with textile materials containing active hydrogen atoms, such as natural cellulose and regenerated cellulose, wool, silk and synthetic polyamide fibers.

According to the invention, the applicant provides coloring agents which are made soluble in water by the presence of sulfonic acid or carboxylic acid groups and which contain, attached on a carbon atom of the coloring agent, a group corresponding to formula (1) hereafter:



in which R represents a hydrogen atom or an alkyl, substituted alkyl, aryl or substituted aryl group, a cycloalkyl or aralkyl radical; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can represent, independently from one another, hydrogen or lower alkyl groups, "n" has a value of 1 or 2, and -CO.Y [sic] represents the radical of a carboxylic monoacid.

As examples of alkyl radicals which can be represented by R in the preceding formula (1), it is possible to mention in particular the lower alkyl radicals such as methyl, ethyl, propyl and butyl.

As examples of substituted alkyl radicals which can be represented by R in the preceding formula (1), it is possible to mention substituted lower alkyl radicals, preferably lower acyloxyalkyl radicals in which the acyl group is identical to that represented by -CO.Y. Thus, when Y represents a methyl, R can represent, for example, beta-acetoxyethyl, gamma-acetoxypropyl or beta,gamma-diacetoxypropyl.

As examples of aryl radicals which can be represented by R in the preceding formula (1), it is possible to mention monocyclic hydrocarbon radicals such as phenyl and tolyl, and as examples of substituted aryl radicals which can be represented by R in the preceding formula (1), it is possible to mention radicals of the benzene series such as chlorophenyl.

As examples of cycloalkyl radicals, it is possible to mention cyclohexyl, and as an example of aralkyl radicals, it is possible to mention benzyl.

As examples of lower alkyl groups which can be represented by R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> in the preceding formula (1), it is possible to mention methyl and ethyl.

As examples of radicals of carboxylic monoacids represented by CO.Y in the preceding formula (1), it is possible to mention those in which Y represents, for example, hydrocarbon radicals, for example, alkyl radicals such as methyl, ethyl, normal propyl and isopropyl; alkenyl radicals such as vinyl and alpha-methylvinyl and beta-methylvinyl; cycloalkyl radicals such as cyclohexyl; aralkyl radicals such as benzyl and naphthylmethyl; aryl radicals such as phenyl and tolyl, and substituted hydrocarbon radicals such as, for example, lower haloalkyl radicals such as chloromethyl, dichloromethyl and beta-dichloropropyl; lower acylalkyls such as acetylmethyl and radicals of the benzene series such as methoxyphenyl, nitrophenyl and chlorophenyl.

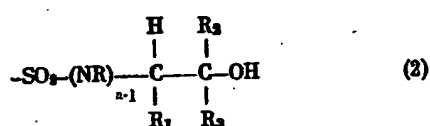
The group corresponding to the preceding formula (1) is attached on a carbon atom of the coloring agent. This atom can, for example, be part of a carbocyclic or heterocyclic aromatic ring, or it can itself be attached on an aromatic ring of the coloring agent directly or by a chain of

atoms (which are not all necessarily carbon atoms) and which can be part of a nonaromatic ring. Said carbon atom is preferably part of a benzene ring which can itself be part of or not part of a polycyclic ring. Thus, in the anthraquinone or phthalocyanine series, said carbon atom can be one of the carbon atoms in the alpha position of the anthraquinone ring or one of the carbon atoms in position 3 or 4 of a phthalocyanine ring, or in the two aforementioned series, it can be one of the carbon atoms of a benzene ring connected with one of these rings, as in a tetraphenylphthalocyanine, a phenylsulfamylphthalocyanine or an alpha-anilinoanthraquinone.

The new coloring agents contain coloring agents of any of the water-soluble species. Thus, just as the members of the anthraquinone and phthalocyanine series mentioned above, the new coloring agents contain members of the nitro and triphenyldioxazine coloring agent series and preferably, members of the azo series, including the monoazo and polyazo coloring agents.

The coloring agents can be free of metals or can contain metals; for example, copper, nickel, cobalt or chromium can be present in the form of complexes in members of the azo or phthalocyanine series.

As another characteristic of the present invention, the applicant proposes a process for the manufacturing of the new coloring agents of the invention, according to which one treats, with a carboxylic monoacid with formula  $Y.CO_2H$  or one of its derivatives which can be used as acylating agent such as the anhydride or the halide of such an acid, a coloring agent which is made soluble in water by the presence of a sulfonic acid or carboxylic acid group and which contains, attached on a carbon atom of the coloring agent, a group corresponding to formula (2) hereafter:



in which  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and "n" have the meaning defined in the preceding.

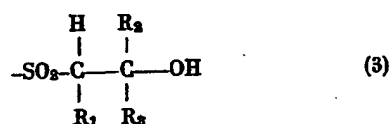
As examples of carboxylic monoacids with formula  $Y.CO_2H$ , it is possible to mention acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, crotonic acid, benzoic acid, chloroacetic acid, methoxybenzoic acid, nitrobenzoic acid, chlorobenzoic acid, phenylacetic acid, toluic acid, cyclohexanecarboxylic acid, dichloroacetic acid, trichloroacetic acid, beta-chloropropionic acid and acetoacetic acid.

The coloring agents which contain the group with the preceding formula (2) can be obtained by a certain number of processes. For example, when  $n = 1$  in the formula, it is possible to obtain suitable coloring agents by transforming a coloring agent containing one or more

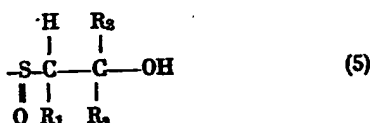
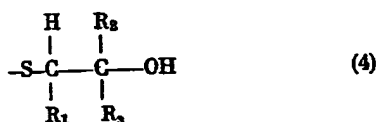
chloride or sulfonyl groups into the corresponding sulfinic acid, or into an alkaline metal salt of such an acid, and by then reacting this product with beta-chloroethyl alcohol or with ethylene oxide. In this way, one obtains compounds containing the group:



If instead of the beta-chloroethyl alcohol or ethylene oxide, one uses compounds containing the appropriate lower alkyl substituents such as beta-chloropropanol, propylene oxide, 1,2-butylene oxide or their lower alkyl derivatives, one obtains products containing group (3) hereafter:



It is also possible to obtain starting materials of this type by subjecting a coloring agent containing group (4) or group (5) hereafter to oxidation:



When the symbol "n" represents the value 2 in the preceding formula (2), it is possible to obtain the coloring agents used as raw materials in the process of the present invention by reacting a coloring agent containing one or more sulfonyl chloride groups with a beta-hydroxyalkylamine such as ethanolamine, N-methylethanolamine, N-ethylethanolamine, N-propylethanolamine and N-butylethanolamine, N-phenylethanolamine, N-tolyethanolamine, N-(chlorophenyl)ethanolamine, N-cyclohexylethanolamine and N-benzylethanolamine, diethanolamine, N-(beta,gamma-dihydroxypropyl)ethanolamine and gamma-hydroxypropyl-beta-hydroxyethylamine.

It is also possible to obtain coloring agents which are intended to be used as starting materials in the aforementioned process of the present invention by formation from intermediate

compounds which can themselves be colored or not, and which already contain the group with the preceding formula (2). In the case of azo coloring agents, said group can be present one or more times in the diazo constituent or in the coupler, or in both; if necessary, the product which is obtained is treated with an agent which gives up metal in order to obtain an azo coloring agent containing a metallic complex. As examples of such agents, it is possible to mention copper, manganese, nickel, zinc and vanadyl sulfates, chromium, cobalt and ferric chlorides, cuproammonium sulfate, chromium acetate, cobalt tartarate and chromium salicylate.

As examples of diazo constituents containing a group corresponding to the preceding formula (2), it is possible to mention para-beta-hydroxyethylsulfonylaniline; 2-amino-4-beta-hydroxyethylsulfonylphenol; 5-beta-hydroxyethylsulfonylaniline-2-sulfonic acid; 5-beta-hydroxyethylsulfamylaniline-2-sulfonic acid; 2-amino-4-beta-hydroxyethylsulfamylphenol; 2-amino-4-(N-beta-hydroxyethyl-N-methylsulfamyl)phenol; 2-amino-4-(N-beta-hydroxyethyl-N-ethylsulfamyl)phenol; 2-amino-4-(N-beta-hydroxyethyl-N-propylsulfamyl)phenol; 2-amino-5-beta-hydroxyethylsulfonylphenol; 2-amino-5-(N-beta-hydroxyethyl-N-ethylsulfamyl)phenol; 4-(beta-hydroxyethylsulfonyl)-anthranilic acid; 2-chloro-5-beta-hydroxyethylsulfonylaniline; 2-amino-4-(N-beta-hydroxyethyl-N-phenylsulfamyl)phenol; 2-amino-4-(N-beta-hydroxyethyl-N-2'-chlorophenylsulfamyl)phenol; m- and p-aminobenzenesulfon-N-beta-hydroxyethylamide; p-aminobenzenesulfon-N-(alpha,beta-dimethyl-beta-hydroxyethyl)amide; p-aminobenzenesulfon-N-(alpha-methyl-beta-hydroxyethyl)amide; 4-amino-3-chlorobenzenesulfon-N-beta-hydroxyethylamide; 2-amino-5-nitrobenzenesulfon-N-beta-hydroxyethylamide; 4-amino-3-chlorophenyl-beta-hydroxyethylsulfone, 4-amino-1-naphthyl-beta-hydroxyethylsulfone and 3-beta-hydroxyethylsulfonylmethyl-4-methylaniline.

These diazo constituents can be coupled with couplers which do not contain a group with the preceding formula (2), for example, with amines, coupling in the para position, of the benzene or naphthalene series, such as 4-sulfo-1,3-phenylenediamine; N,N-dimethylaniline; N,N-diethylaniline; N,N-diethyl-m-toluidine; N-ethyl-N-beta-hydroxyethylaniline; N,N-di-(beta-hydroxyethyl)-m-toluidine; N-ethyl-N-beta-cyanoethylaniline; N-beta-hydroxyethyl-N-beta-cyanoethylaniline; N,N-di(beta-acetoxyethylaniline); N,N-di-(beta-carboethoxyethyl)aniline; N-(beta-cyanoethyl-N-beta-methoxyethylaniline); 3-N,N-di(beta-acetoxyethyl)aminoacetanilide; N-beta-hydroxyethylaniline and N-beta-hydroxyethyl-1-naphthylamine; other amines coupling in the ortho position, such as

1-naphthylamine-4-sulfonamide; 2-naphthylamine-6-sulfonamide and 4-chloronaphthylamine; phenols such as 1-phenol-4-sulfonic acid; p-cresol; 3,4- or 2,4-dimethylphenol; 2- or 3-acetyl-amino-4-methylphenol; t-butylphenol; 4-thiocyanophenol; 4-sulfamylphenol, 4-acetylphenol; 2-hydroxy-5,6,7,8-tetrahydronaphthalene; 2-hydroxy-3-sulfamyl-5,6,7,8-tetrahydronaphthalene; 4-methoxyphenol; 2-carboethoxyamino-4-methylphenol; o and p-phenylphenol; 2-hydroxydiphenylene oxide and 2,4-dihydroxyquinoline, naphthols and naphthosulfonic acids such as 2-naphthol; acetyl-amino-; 1-propionyl-amino-, 1-benzenesulfonyl-amino-, 1-carbomethoxyamino-, 1-carboethoxyamino-, 1-carboisopropyl-amino- and 1-phenyl-amino-7-naphthols; 6-acetyl-2-naphthol, 4-acetyl-1-naphthol; 1-naphthol-3- 4- or 5-sulfonamide; 2-naphthol-3-, 4-, 5-, 6-, 7- or 8-sulfonamide; 5,8-dichloro-1-naphthol; 5-chloro-1-naphthol; 1,5-dihydroxynaphthalene, 1-acetyl-amino-4-, 5- or 6-naphthol and 2-acetyl-amino-7-naphthol; 1-naphthol-4- and 5-sulfonic acids; 2-naphthol-6-, -7- and -8-sulfonic acids; 1-naphthol-3,6- and 3,8-disulfonic acids; the 2-naphthol-3,6- and 6,8-disulfonic acids; 1-naphthol-3,6,8-trisulfonic acid; 1,8-dihydroxynaphthalene-3,6-disulfonic acid; 2-acetyl-amino-5-naphthol-7-sulfonic acid; 2-acetyl-amino-8-naphthol-6-sulfonic acid and 1-acetyl-amino-8-naphthol-3,6 and 4,6-disulfonic acids; aminonaphthols and aminonaphtholsulfonic acids such as 1,8-aminonaphthol-6-sulfonic acid; 1,8-aminonaphthol-3,6 and 4,6-disulfonic acids; 2,5-aminonaphthol-7-sulfonic acid; 2,8-aminonaphthol-6-sulfonic acid; 2,5-aminonaphthol-1,7-disulfonic acid; 2,8-aminonaphthol-3,6-disulfonic acid; the 1-amino-6-naphthol-3-, 4- and -8-sulfonic acids and their lower N-alkyl derivatives such as 1-butyl-amino-8-naphthol-3,6-disulfonic acid and 2-methyl-amino-5-naphthol-7-sulfonic acid and their N-aryl derivatives such as 1-phenyl-amino-8-naphthol-3,6-disulfonic acid; ketomethylene compounds such as 1-(2'-methoxyphenyl)-3-methyl-5-pyrazolone; 1-phenyl-3-methyl-5-pyrazolone; 1-(2'-, 3'- or 4'-methylphenyl)-3-methyl-5-pyrazolone; 1-(2'-, 3'- or 4'-chlorophenyl)-3-methyl-5-pyrazolone; 1-(2'-, 3'- or 4'-nitrophenyl)-3-methyl-5-pyrazolone; 1-(2',5'- or 3',4'-dichlorophenyl)-3-methyl-5-pyrazolone; 1-(2'- 3'- or 4'-sulfamylphenyl)-3-methyl-5-pyrazolone; 3-methyl-5-pyrazolone; 1-(2'-, 3'- or 4'-methylsulfonylphenyl)-3-methyl-5-pyrazolone; 1-phenyl-5-pyrazolone-3-carboxycresidide [sic]; 1-phenyl-5-pyrazolone-3-carboxy-2'-toluidide; 1-phenyl-5-pyrazolone-3-carboxyanilide; 1,3-diphenyl-5-pyrazolone; 1-(2'-, 3'- or 4'-N-methylsulfamylphenyl)-3-methyl-5-pyrazolone; 1-(2'-, 3'- or 4'-N,N-diethylsulfamylphenyl)-3-methyl-5-pyrazolone; acetoacetanilide; acetoacet-o-anisidide, and acetoacetanilide-4-sulfonamide; 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone; 1-(6'-chloro-3'-methyl-4'-sulfophenyl)-3-methyl-5-pyrazolone; 1-(2',5'-dichloro-4'-sulfophenyl)-3-methyl-5-pyrazolone; 1-(2'-methyl-5'-sulfophenyl)-3-methyl-5-pyrazolone;

1-(2'-chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(4'-chloro-2'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(2'-chloro-4'-methyl-5'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(6'-chloro-4'-sulfo-2'-methylphenyl)-3-carboethoxy-5-pyrazolone;  
 1-(6'-chloro-4'-sulfo-2'-methylphenyl)-3-methyl-5-pyrazolone;  
 1-(4'-methyl-2'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(2',5'-disulfophenyl)-3-methyl-5-pyrazolone;  
 1-(4'-ethoxy-2'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(2',4'-dichloro-5'-sulfophenyl)-3-methyl-5-pyrazolone;  
 1-(6'-chloro-3'-sulfo-2'-phenyl)-3-methyl-5-pyrazolone;  
 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone; 1-(3',5'-disulfophenyl)-3-methyl-5-pyrazolone;  
 1-(4'-carboxyphenyl)-3-methyl-5-pyrazolone; 1-(3'-carboxyphenyl)-3-methyl-5-pyrazolone;  
 1-(2'-carboxyphenyl)-3-methyl-5-pyrazolone; 1-phenyl-3-carboxy-5-pyrazolone;  
 1-p-tolyl-3-carboxy-5-pyrazolone; 3-carboxy-5-pyrazolone.

As examples of couplers which contain a group with the preceding formula (2), it is possible to mention, for example, 6-beta-hydroxyethylsulfonyl-2-naphthol-3-sulfonic acid; 2-naphthol-6-beta-hydroxyethylsulfone; 1-naphthol-4-beta-hydroxyethylsulfone; 1-(3'- or 4'-beta-hydroxyethylsulfonylphenyl)-3-methyl-5-pyrazolone; m-(N,N-diethylamino)benzenesulfon-N-beta-hydroxyethylamide; m-(N,N-dimethylamine)benzenesulfon-N-beta-hydroxyethylamide, m-(N,N-diethylamino)phenyl-beta-hydroxyethylsulfone; 1-(3'- or 4'-beta-hydroxyethylsulfamoylphenyl)-3-methyl-5-pyrazolone; 2-naphthol-6-beta-hydroxyethylsulfonamide; 2-naphthylamino-6-sulfon-beta-hydroxyethylamide and 6-beta-hydroxyethylsulfonyl-2-naphthylamine.

As a variant, it is possible to couple these couplers with diazo constituents which do not contain groups with the preceding formula (2), such as, for example, diazotizable amines of the benzene series, such as, for example, aniline, o-, m- and p-toluidine, o-, m- and p-anisidine, m and p-nitroaniline; m- and p-aminoacetanilide, orthoanilic acid, metanilic acid, sulfanilic acid, aniline-2,4-, 2,5- and 3,5-disulfonic acids; 4-methylaniline-2-sulfonic acid; 5-methylaniline-2-sulfonic acid; 2-methylaniline-5-sulfonic acid; 2,4-dimethylaniline-6-sulfonic acid, 4-methylaniline-2,5-, 3,5- and 2,6-disulfonic acids; 2-methylaniline-4,6-disulfonic acid; 5-chloro-2-aminoanisole; 4-methoxyaniline-2-sulfonic acid; 5-methoxyaniline-2-sulfonic acid; 2-methoxyaniline-5-sulfonic acid; 2,4-dimethoxyaniline-6-sulfonic acid; 4-chloroaniline-2-sulfonic acid; 4,5-dichloroaniline-2-sulfonic acid; 2,5-dichloroaniline-4-sulfonic acid; 4-acetylaminoaniline-2-sulfonic acid; 5-acetylaminoaniline-2-sulfonic acid; 2-trifluoromethylaniline;



4-trifluoromethylaniline-2-sulfonic acid; 4-chloro-5-methylaniline-2-sulfonic acid;  
 3-chloro-2-methylaniline-4,6-disulfonic acid; 5-chloro-4-methylaniline-2-sulfonic acid;  
 4-nitroaniline-2-sulfonic acid; 5-nitroaniline-2-sulfonic acid;  
 4-nitro-2-methoxyaniline-5-sulfonic acid; 5-amino-2-methylacetanilide-4-sulfonic acid;  
 aniline-2-, -3- and -4-carboxylic acids and their esters such as methyl and butyl anthranilates;  
 2-aminophenol; 2-aminophenol-4-sulfonic acid; 2-aminophenol-4,6-disulfonic acid;  
 4-ethanesulfonyl-2-aminophenol; 3-amino-4-hydroxyacetophenone;  
 4-nitro-2-aminophenol-6-sulfonic acid; 6-nitro-2-aminophenol-4-sulfonic acid;  
 4-chloro-2-aminophenol-6-sulfonic acid; 6-chloro-2-aminophenol-4-sulfonic acid, 4- and  
 5-nitro-2-aminophenols; 4,6-dinitro-2-aminophenol; 4-, 5- or -6-chloro-2-aminophenol;  
 4-sulfamyl-2-aminophenol; 4-methylsulfamyl-2-aminophenol; 4- and 5-sulfo-2-aminobenzoic  
 acids; aminoterephthalic acid; 4-aminoisophthalic acid; 5-nitro-2-aminophenoxyacetic acid;  
 5-chloro-2-aminobenzoic acid; 5-nitro-2-aminobenzoic acid and 2-sulfamylaniline;  
 2-ethylsulfamylaniline; 2-aminophenylethylsulfone; 4- and 5-aminosalicylic acids.

Diazotizable amines of the naphthalene series and other compounds with condensed rings  
 such as 1- and 2-naphthylamine; 1-naphthylamine-4-, 5-, 6- and 7-monosulfonic acids; the  
 2-naphthylamine-1, 6-, 7- and 8-monosulfonic acids; 1-naphthylamine-2,4-, 2,5-, 3,6- and  
 3,8-disulfonic acids; 2 naphthylamine-1,5-, 3,6-, 4,8-, 5,7- and 6,8-disulfonic acids;  
 1-naphthylamine-2,4,6- and 2,5,7-trisulfonic acids; 2-naphthylamine-1,5,7- and 3,6,8-trisulfonic  
 acids; 2-methoxy-1-naphthylamine-6- and -7-sulfonic acids, 1-amino-2-naphthol-4-sulfonic acid;  
 1-amino-6-nitro-2-naphthol-4-sulfonic acid; 1- and 2-aminoanthraquinone;  
 1-aminopyrenemonosulfonic acid; 3-aminochrysenesulfonic acid.

Diazotizable amines containing more than one noncondensed phenyl ring, such as  
 4-aminophenyl-3- and 4'-sulfonic acids; 4'-nitro-4-aminostilbene-2,2'-disulfonic acid;  
 4'-acetyl-amino-4-aminostilbene-2,2'-disulfonic acid; 4'-benzoylamino-4-aminostilbene-  
 2,2'-disulfonic acid; 4'-chloro-4-aminostilbene-2,2'-disulfonic acid; 4'-bromo-4-aminostilbene-  
 2,2'-disulfonic acid; 4'-dimethylamino-4-aminostilbene-2,2'-disulfonic acid;  
 4'-anilino-4-aminostilbene-2,2'-disulfonic acid; 2-amino-2'-methyldiphenyl ether and its sulfonic  
 acid at 4' position; 2-aminodiphenylsulfone; 4-aminodiphenylamine;  
 4-amino-4'-nitrodiphenylamino-2'-sulfonic acid; 3- and 4-aminobenzanilides; 3'- and  
 4'-aminobenzanilides; 3'- and 4'-aminobenzanilide-3- and 4-sulfonic acids.

Also, heterocyclic amino compounds such as 4-aminoindazole, 5-aminoindazole, and  
 6-aminoindazole; 6-amino-5-methoxy-2-(4'-sulfophenyl)benzo-1,2,3-triazole,  
 6-methyl-2-(4'-aminophenyl)benzothiazole and its products of monosulfonation or disulfonation,  
 2-(4'-aminophenyl)naphtha-1,2,3-triazole-3',5-disulfonic acid, 2-(3' and  
 4'-aminophenyl)naphtha-1,2,3-triazole-4,7,9-trisulfonic acids, 2-(4'-aminophenyl)naphtha-

1,2,3-triazole-3',4,7,9-tetrasulfonic acid, 5-nitro-2-aminothiazole and 3-aminopyridine.

It is possible to obtain the anthraquinone coloring agents which can be used as starting materials for the aforementioned process of the present invention by condensing, for example, an anthraquinone containing a halogen atom in the alpha position with an amine, and preferably an aromatic amine containing a group with the preceding formula (2); thus, for example, it is possible to condense 1-amino-4-bromoanthraquinone-4-sulfonic acid with 3- or 4-beta-hydroxyethylsulfonylaniline or with a beta-hydroxyethylsulfamylaniline.

It is also possible to obtain coloring agents of the ortho-nitrodiphenylamine series which can be used as starting materials in the aforementioned process of the invention, by condensing, for example, an ortho-halonitrobenzene with an aromatic primary amine of the benzene series, one of the reagents containing a group with formula (2) and the second containing a carboxylic acid or sulfonic acid group. Thus, it is possible to condense 4-chloro-3-nitrophenyl-beta-hydroxyethylsulfone with, for example, metanilic acid, meta-aminobenzoic acid or derivatives of these acids substituted on the ring, or else it is possible to condense meta-beta-hydroxyethylsulfonylaniline with, for example, 4-chloro-3-nitrobenzoic acid or 4-chloro-3-nitrobenzenesulfonic acid.

It is also possible to obtain coloring agents of the phthalocyanine series which can be used as starting materials in the aforementioned process of the invention, by condensing, for example, an amine, and preferably an aromatic amine, containing a group with the preceding formula (2), with a phthalocyanine sulfonyl chloride.

It is understood that in all these processes for obtaining coloring agents suitable for use as starting materials for the aforementioned process of the invention, the intermediates are chosen so as to finally obtain a coloring agent which contains one or more sulfonic acid or carboxylic acid groups.

The aforementioned process of the present invention can be implemented conveniently by stirring together the anhydride or halide of the acid with formula Y.COOH and the coloring agent containing at least one group with the preceding formula (2) in a liquid tertiary amine or in an organic liquid in the presence of a tertiary amine, preferably at a temperature between 0 and 50°C, and when the reaction is finished, by adding a liquid, such as water or diethyl ether or an aqueous sodium chloride solution, which is a solvent of the tertiary amine and/or of the organic liquid, but in which the coloring agent is insoluble, and by separating the precipitated coloring agent by filtration.

As examples of acid anhydrides or halides which can be used in the aforementioned process of the invention, it is possible to mention acetic anhydride, acetyl chloride, acetyl bromide, propionyl chloride, butyryl chloride, alpha-chloroacetyl chloride, benzoyl chloride, benzoyl bromide, methoxybenzoyl chloride, chlorobenzyl chloride, beta-chloropropionyl

chloride, alpha-bromoacetyl bromide, acryloyl chloride, alphaphenylacetyl chloride and nitrobenzyl chloride.

It is also possible to obtain the new coloring agents of the invention by reacting together intermediate coloring agents which already contain the group with the preceding formula (1) and which are chosen so as to give products containing sulfonic acid or carboxylic acid groups, and this process which is indicated as a variant constitutes another characteristic of the invention. These sulfonic acid or carboxylic acid groups can be present in the intermediate compound or else can be formed, for example, by hydrolysis of the sulfonyl chloride or carbonyl chloride groups done simultaneously with the formation of the coloring agent.

For example, it is possible to obtain azo coloring agents containing at least one group with formula (1) by diazotizing a primary aromatic amine, which can be an aminoazo compound, and by coupling the diazo compound thus obtained with a coupler, the aromatic primary amine or the coupler or the two containing at least one group with formula (1), and the primary amine or the coupler or the two containing at least one sulfonic acid or carboxylic acid group.

Said aromatic primary amine is preferably an aromatic primary amine of the benzene or naphthalene series, which is optionally substituted by an arylazo radical, and which can contain or not contain a group with formula (1), as defined in the preceding. It is possible to obtain these aromatic primary amines containing a group with formula (1) by treating the corresponding nitro compounds containing a group with formula (2) with an anhydride or a halide of an acid with formula  $Y.CO_2H$ , and by then reducing the nitro group to an amino group. Particular examples of aromatic primary amines containing a group with formula (2) have already been indicated in the present disclosure.

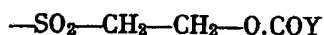
Said couplers can be members of any of the known series of couplers, but they are preferably couplers of the acylacetylride, 5-pyrazolone, phenol, naphthol or arylamine series which possibly contain a group with formula (1). It is possible to obtain such couplers containing a group with formula (1) by treating the corresponding couplers containing a group with formula (2) with an anhydride or a halide of an acid with formula  $Y.CO_2H$ . Particular examples of couplers containing a group with formula (2) have already been indicated in the present disclosure. As particular examples of couplers containing a group with formula (1), it is possible to mention 4-beta-acetoxyethylsulfonyl-1-naphthol and 6-beta-acetoxyethylsulfonyl-2-naphthol-3-sulfonic acid.

As a variant, it is possible to condense aromatic primary amines containing a group with formula (1) attached directly or by the intermediary of a methylene group on an aryl ring present in said amine, with coloring agents or coloring agent intermediates containing reactive halogen atoms such as the alpha-halogenated anthraquinones and the phthalocyaninesulfonyl or phthalocyanine carbonyl chlorides.

As examples of aromatic primary amines which can contain a group with formula (1) attached directly or by the intermediary of a methylene on an aryl ring present in said amines, it is possible to mention 2-chloro-5-beta-acetoxyethylsulfonylaniline, 4-beta-acetoxyethylsulfonylaniline, 3-beta-acetoxyethylsulfonylaniline, 4-beta-acetoxyethylsulfonylaniline, 3-(beta-acetoxyethylsulfonylmethyl)-4-methylaniline, 2-methoxy-5-beta-acetoxyethylsulfonylaniline, 5-beta-acetoxyethylsulfonylaniline-2-sulfonic acid and 2-amino-4-beta-acetoxyethylsulfonylphenol.

As examples of coloring agents or coloring agent intermediates containing reactive halogen atoms and which can be reacted with these primary aromatic amines, it is possible to mention phthalocyanine sulfonyl chlorides and in particular (copper phthalocyanine) sulfonyl chlorides, 4-chloro-3-nitrobenzenesulfonic acid, alpha-haloanthraquinonesulfonic acids such as 1-amino-4-bromoanthraquinone-2-sulfonic acid, 1-amino-4-bromoanthraquinone-2,5-, 2,6-, 2,7- and 2,8-disulfonic acids, 1-amino-2,4-dibromoanthraquinone-5-, 6-, 7- and 8-sulfonic acids, 1,4-bis(para-phenylaniline)anthraquinonetetrasulfonyl chloride and 4-chloro-3-nitrobenzoic acid.

A preferred class of the new coloring agents, as defined in the preceding, is that of the coloring agents which contain at least one sulfonic acid or carboxylic acid group and which contain 1 or 2 groups with formula:



in which Y has the meaning defined in the preceding. The applicant however prefers that Y represent a lower alkyl radical or a monocyclic aryl radical.

The new coloring agents, as defined in the preceding, are advantageous for dyeing natural and artificial textile materials containing cotton, viscose rayon, regenerated cellulose, wool, silk, cellulose acetate, polyamides, polyacrylonitrile, modified polyacrylonitrile and fibers of aromatic polyesters. For this purpose, it is possible to apply the coloring agents to the textile materials by painting, padding or printing using printing pastes containing the conventional thickeners or using oil-in-water emulsions or water-in-oil emulsions, coloring the textile material vivid shades with excellent fastness with regard to wet treatments such as washing. The new coloring agents fasten well onto textile material giving deep color shades.

The new coloring agents are particularly advantageous for coloring the cellulose-containing textile materials. For this purpose, the coloring agents are preferably applied to the cellulose textile material along with treatment with an acid fixing agent, such as, for example, sodium carbonate, sodium metasilicate, trisodium phosphate or sodium hydroxide, which can be applied to the cellulose textile material before, during or after the application of the

coloring agent. As a variant, if one wishes later to heat the dyed textile material or subject it to steaming, it is possible to use a substance which, like sodium bicarbonate or sodium trichloroacetate, releases an acid fixing agent by heating or steaming.

For example, it is possible to color the cellulose textile material by treating this cellulose textile material with an aqueous solution or suspension of the acid fixing agent and by then immersing the cellulose textile material thus treated in a dyeing fluid consisting of a solution of one or more coloring agents, as defined in the preceding, at a temperature between 0 and 100°C, by removing the dyed cellulose textile material from the dyeing fluid, and if desired, by subjecting the dyed cellulose textile material to a treatment in a hot aqueous soap solution.

If desired, the cellulose textile material, which has been treated with an aqueous solution or suspension of an acid fixing agent, can be run between rollers in order to eliminate the excess aqueous solution or suspension of acid fixing agent and/or this textile material can be dried before treatment with the aqueous solution of said coloring agents.

As a variant, the aqueous solution of the coloring agent can be applied to the cellulose textile material which has been treated with the acid fixing agent by padding, and the cellulose textile material can then be run between rollers and then subjected to the action of heat or steam. As a variant, it is possible to pad the cellulose textile material with an aqueous solution of one or more of the new coloring agents, as defined in the preceding, this solution also containing an acid fixing agent, to run the cellulose textile material thus treated between rollers and then, if desired, to dry this cellulose textile material at an appropriate temperature, for example, 70°C, and then to subject the cellulose textile material to the action of heat or steam. As a variant, it is possible to dye the cellulose textile material by immersing it in a dyeing fluid consisting of an aqueous solution of one or more of said coloring agents, this fluid also containing an acid fixing agent, at an appropriate temperature between, for example, 0 and 100°C, by then removing the cellulose textile material from the dyeing fluid, by subjecting it if desired to a treatment in a hot aqueous soap solution and finally by drying the dyed cellulose textile material. It is also possible to apply the aqueous solution of one or more of said coloring agents to the cellulose textile material by a dyeing or padding process and to immerse the colored cellulose textile material in an aqueous solution or suspension of an acid fixing agent, preferably at a temperature between 50 and 100°C, or as a variant, it is possible to pad the colored cellulose textile material by means of an aqueous solution or suspension of the acid fixing agent, to dry the textile material and then to subject it to the action of heat or steam. As a variant, it is possible to dye the cellulose textile material by immersing it in a dyeing fluid consisting of an aqueous solution of one or more of said coloring agents, preferably at a temperature between 20 and 100°C, and after the textile material has absorbed part or all of the coloring agents, to add an acid fixing agent and to continue the dyeing at the same temperature or at a different temperature.

The concentration of the acid fixing agent present in the aqueous solution or suspension of acid fixing agent or present in the aqueous solution of coloring agent is not critical, but the applicant prefers to use between 0.1 and 10% acid fixing agent with respect to the total weight of the aqueous solution or suspension. If desired, the aqueous solution or suspension of acid fixing agent can also contain other substances, for example, electrolytes such as sodium chloride and sodium sulfate.

The aqueous solution of said coloring agents can also contain substances which are known to aid in the application of the coloring agent to the textile materials, for example, sodium chloride, sodium sulfate, urea, dispersants, surfactants, sodium alginate or an emulsion of an organic liquid, for example, trichloroethylene in water.

As a variant, it is possible to print the cellulose textile materials with a printing paste containing one or more of the new coloring agents of the invention.

It is possible to operate conveniently by applying a printing paste containing one or more of said coloring agents to a cellulose textile material which has been impregnated with an acid fixing agent and by then subjecting the printed cellulose textile material to the action of heat or steam. As a variant, it is possible to apply a printing paste containing one or more of said coloring agents and containing an acid fixing agent to the cellulose textile material, and it is then possible to subject the printed cellulose textile material to the action of heat or steam. As a variant, it is possible to apply a printing paste containing one or more of said coloring agents to the cellulose textile material which is then immersed in a hot aqueous solution or suspension of acid fixing agent and which is then subjected to the action of heat or steam.

After application of the printing paste to the cellulose textile material, it is possible if desired to dry the printed textile material, for example, at a temperature between 20 and 100°C before subjecting the printed textile material to the action of heat or steam.

It is possible to print the cellulose textile material by means of a printing paste by any of the commonly known processes for application of printing pastes on textile materials, for example, by roller printing, screen printing, plate printing, spray printing and printing with a stencil. The printing pastes can also contain the conventionally used additives such as, for example, urea; thickeners, for example, methylcellulose, starch, locust-bean gum, sodium alginate, water-in-oil type emulsions, oil-in-water type emulsions, surfactants, sodium meta-nitrobenzenesulfonate; and organic liquids, for example, ethanol.

At the end of the dyeing and/or printing processes, the applicant prefers to subject the cellulose textile materials thus colored to a "soaping" treatment which can be conducted by immersing the colored cellulose textile materials for a brief duration of 15 min, for example, in a hot aqueous soap and/or detergent solution and by then rinsing the colored cellulose textile material in water before drying this material.

The new coloring agents as defined in the preceding are also advantageous for coloring textile materials containing nitrogen such as wool and polyamide textile materials, and in order to color these textile materials, the applicant prefers to apply the coloring agents in a slightly alkaline, neutral or acidic dyeing fluid. It is possible to carry out the dyeing process at a constant or practically constant pH, that is to say that the pH of the fluid remains constant or practically constant during the dyeing operations, or if desired, the pH of the dyeing fluid can be modified at any time in the dying process by adding acids or acid salts or alkaline bases or alkaline salts. For example, it is possible to begin the dyeing with a dyeing fluid pH of approximately 3.5-5.5, and during the dyeing process, to bring the value of the pH to approximately 6.5-7.5 or higher if desired. The dyeing fluid can also contain substances which are commonly used for dyeing of textile materials containing nitrogen. As examples of such substances, it is possible to mention ammonium acetate, sodium sulfate, ethyl tartarate, nonionic dispersants such as condensates of ethylene oxide with amines of fatty alcohols or phenols, cationic surfactants such as quaternary ammonium salts such as, for example, cetyltrimethylammonium bromide and cetylpyridinium bromide and organic liquids such as normal butanol and benzyl alcohol.

The applicant assumes that the new coloring agents as defined in the preceding, once applied to the textile materials, react with hydroxy and/or amino groups present in said textile materials, causing the fixing of these coloring agents to the textile materials by chemical bonds, this opinion being based on the resistance of the resulting coloring agents to severe washing treatments and also to treatments of extraction by solvent.

The invention is illustrated but not limited by the following examples in which the parts and percentages are in terms of weight.

#### Example 1

27.75 parts of 2-chloro-5-beta-acetoxyethylsulfonylaniline are dissolved in a mixture of 25 parts of a concentrated aqueous hydrochloric acid solution and 500 parts water. The solution is cooled to 2°C, and while stirring, a solution of 6.9 parts sodium nitrite in 60 parts water is added. The mixture is stirred for 15 min, and sodium bicarbonate is added until the mixture is no longer acidic with Congo Red [used as the pH indicator]. While stirring, the diazo solution thus obtained is added to a solution of 21.12 parts 2-naphthol-6-sulfonic acid, 4.4 parts sodium hydroxide and 20 parts sodium carbonate in 200 parts water which has been cooled to 2°C. The mixture is stirred for 4 h, and 100 parts sodium chloride are added. The coloring agent which precipitates is separated by filtration, it is washed with a 10% aqueous salt solution, and finally it is dried. It dyes cellulose to orange shades.

It is possible to obtain the 2-chloro-5-beta-acetoxyethylsulfonylaniline used in the example above by reacting 1-chloro-2-nitro-4-beta-hydroxyethylsulfonylbenzene with acetic anhydride in pyridine, adding water, and isolating the 1-chloro-2-nitro-4-beta-acetoxyethylsulfonylbenzene and by reducing the nitro group to an amine group by treating a solution of the nitro compound in ethanol with hydrogen in the presence of Raney nickel as a catalyst.

### Example 2

12 parts of 1-amino-4-(3'-beta-hydroxyethylsulfonylanilino)anthraquinone-2-sulfonic acid are dissolved in 60 parts dry pyridine. The solution is cooled to 0°, and 7.6 parts acetic anhydride are added. This mixture is stirred for 4 h between 0 and 4°C and is then filtered. The mixture is stirred on the filter in diethyl ether, it is then refiltered and washed with diethyl ether and then dried.

The product obtained is the pyridine salt of 1-amino-4-(3'-beta-acetoxyethylsulfonylanilino)anthraquinone-2-sulfonic acid. It can be obtained in the form of a sodium salt by dissolving it in hot water, by adding sodium bicarbonate until the solution is alkaline and by then adding sodium chloride, which precipitates the coloring agent in the form of a sodium salt.

It dyes cellulose to vivid reddish-blue shades.

The following table (Examples 3-21) gives other examples of new coloring agents of the invention which are obtained when the 27.75 parts of 2-chloro-5-beta-acetoxyethylsulfonylaniline used in Example 1 are replaced by equivalent quantities of the amines listed in the second column of the table and/or the 21.12 parts 2-naphthol-6-sulfonic acid are replaced by equivalent quantities of the couplers listed in the third column of the table. The fourth column of the table indicates the shades obtained when these coloring agents are applied to textile materials.



Exemple ①	Amine	Copulant ②	Teinte ③
3	2 - méthoxy - 5 - bêta - acétoxyéthyl-sulfonylaniline.	1 - (2' - méthyl - 4' - sulfo - 6' - chlorophényl) - 3 - méthyl - 5 - pyrazolone.	Jaune-verdâtre ⑮
4	2 - méthoxy - 5 - bêta - benzoyloxyéthyl-sulfonylaniline.	Acide 1-amino-8-naphtol-3: 6-disulfonique. ④	Violet-rougeâtre ⑯
5	2 - méthoxy - 5 - bêta - acétoxyéthyl-sulfonylaniline.	Acide 2-N-acétylamino-5-naphtol-7-sulfonique ⑤	Orangé ⑰
6	Idem.....	Acide 1-naphtol-5-sulfonique..... ⑥	Rouge ⑱
7	Idem.....	Acide 1-N-phénylamino-8-naphtol-3: 6-disulfonique. ⑦	Cris-Brûlé ⑲
8	Idem.....	Acide 2-N-phénylamino-5-naphtol-7-sulfonique ⑧	Rouge ⑲
9	Idem.....	Acide 1-(3'-amino-4'-sulfophényl)-5-pyrazolone-3-carboxylique. ⑨	Jaune ⑳
10	Idem.....	1-(2'-méthyl-5' - sulfophényl) - 3 - méthyl - 5 - pyrazolone.	Idem
11	2 - méthoxy - 5 - bêta - acétoxyéthyl-sulfonylaniline.	1-(3'-méthyl-4' - sulfo-6' - chlorophényl)-3 - méthyl-5-pyrazolone.	Jaune ㉑
12	Idem.....	Acide 1-phényl-5-pyrazolone-3-carboxylique. ⑩	Idem
13	Idem.....	Acide 1-(3'-nitrophényl)-5-pyrazolone-3-carboxylique. ⑪	Idem
14	Idem.....	1-(2'-méthyl-3' - sulfo-6' - chlorophényl) - 3 - méthyl-5-pyrazolone.	Idem
15	Idem.....	1-(2' - chloro-5' - sulfophényl)3 - méthyl-5-pyrazolone.	Idem
16	Idem.....	1-(2'-méthyl-4' - sulfo-6' - chlorophényl) - 3 - carboéthoxy-5-pyrazolone.	Idem
17	2 - méthoxy - 5 - bêta - benzoyloxyéthyl-sulfonylaniline.	Acide 2-naphtol-3: 6-disulfonique. ⑫	Rouge ㉒
18	Idem.....	1-(2'-méthyl-4' - sulfo-6' - chlorophényl) - 3 - méthyl-5-pyrazolone.	Jaune ㉓
19	2 - chloro - 5 - bêta - acétoxyéthyl-sulfonylaniline.	Acide 1-naphtol-5-sulfonique. ⑬	Rouge blenté ㉔
20	Idem.....	Acide 2-N-acétylamino-5-naphtol-7-sulfonique. ⑭	Orangé ㉕
21	Idem.....	1-(3'-sulfophényl)-3-méthyl-5-pyrazolone....	Jaune ㉖

- Key:
- 1 Example
  - 2 Coupler
  - 3 Shade
  - 4 1-Amino-8-naphtol-3,6-disulfonic acid
  - 5 2-N-Acetylamino-5-naphtol-7-sulfonic acid
  - 6 1-Naphtol-5-sulfonic acid
  - 7 1-N-Phenylamino-8-naphtol-3,6-disulfonic acid
  - 8 2-N-Phenylamino-5-naphtol-7-sulfonic acid
  - 9 1-(3'-Amino-4'-sulfophényl)-5-pyrazolone-3-carboxylic acid
  - 10 1-Phenyl-5-pyrazolone-3-carboxylic acid
  - 11 1-(3'-Nitrophényl)-5-pyrazolone-3-carboxylic acid
  - 12 2-Naphtol-3,6-disulfonic acid

13	1-Naphthol-5-sulfonic acid
14	2-N-Acetylamino-5-naphthol-7-sulfonic acid
15	Greenish yellow
16	Reddish violet
17	Orange
18	Red
19	Brownish gray
20	Yellow
21	Bluish red

### Example 22

46.5 parts of the monosodium salt of 1-(2'-methoxy-5'-beta-hydroxyethylsulfonylphenylazo)-2-naphthylamine-6-sulfonic acid (which is obtained by coupling diazotized 2-methoxy-5-beta-hydroxyethylsulfonylaniline with 2-naphthylamine-6-sulfonic acid under acid conditions) are stirred in 460 parts pyridine at a temperature of 20°C, and 30 parts acetic anhydride are gradually added with the temperature of the mixture maintained at 20°C by external cooling. The resulting mixture is stirred for 16 h at 20°C, 1000 parts water are added, the precipitated coloring agent is separated by filtration, it is washed with benzene and it is dried. Applied to wool in a slightly acidic dyeing fluid, the coloring agent produces vivid orange shades with excellent fastness with regard to wet treatments.

The following table gives other examples (23-49) of new coloring agents of the invention which are obtained by replacing the 46.5 parts monosodium salt of the azo compound used in Example 22 by equivalent quantities of the sodium salts of the azo compounds which are obtained by diazotizing the amine indicated in the second column of the table and by coupling the diazo compounds thus obtained with the couplers listed in the third column of the table, under acid or alkaline conditions as indicated in the fourth column of the table, and/or when the 30 parts acetic anhydride used in Example 22 are replaced by equivalent quantities of acylating [agents] listed in the fifth column of the table. The sixth column of the table indicates the shades obtained when these coloring agents are applied to textile materials.

Exemple (1)	Amine	Copulant (2)	Conditions de (3) copulation	Agent d'acylation (4)	Teinte (5)
23	2 - méthoxy - 5 - bêta - hydroxy - éthylsulfonyl-aniline.	1 - (2' - méthyl - 4' - sulfo - 6' - chlorophényl) - 3 - méthyl - 5 - pyrazolone.	Alcalines (26)	Anhydride acétique (28)	Jaune (33)
24	Idem.....	Acide 1-naphtol-4-sulfonique. (9)	Idem	Idem	Rouge (34)
25	Idem.....	1 - (2' : 5' - dichloro - 4' - sulfo-phényl)-3-méthyl-5-pyrazolone.	Idem	Idem	Jaune (33)
26	2 - méthoxy - 5 - bêta - hydroxyéthylsulfonyl-aniline.	Acide 2-naphtol-6-sulfonique... (10)	Alcalines (26)	Anhydride acétique (28)	Orangé (35)
27	Idem.....	Acide 2-naphtol-7-sulfonique (11)	Idem	Idem	Rouge (36)
28	Idem.....	Idem.....	Idem	Chlorure d'acétyle (29)	orangé Idem
29	Idem.....	Acide 1-naphtol-5-sulfonique (12)	Idem	Anhydride acétique (28)	Rouge (34)
30	Idem.....	Acide 2-amino-5-naphtol-7-sulfonique. (13)	Idem	Idem	Orangé (35)
31	Idem.....	1 - (3' - sulfophényl) - 3 - méthyl - 5 - pyrazolone.	Idem	Idem	Jaune (33)
32	Idem.....	Acide 2-amino-8-naphtol-6-sulfonique. (14)	Acides (27)	Idem	Rouge (34)
33	Idem.....	Acide m-phénylène-diaminesulfonique (15)	Idem	Idem	Jaune (33)
34	Idem.....	Acide 2-N-méthylamino-8-naphtol-6-sulfonique (16)	Alcalines (26)	Idem	Brun (37)
35	2 - méthoxy - 5 - bêta - hydroxyéthylsulfonyl-aniline.	Acide 2-N-acétylamino-5-naphtol-7-sulfonique. (17)	Idem	Anhydride acétique (28)	Orangé (35)
36	Idem.....	Acide m-phénylènediaminesulfonique (18)	Acides (27)	Chlorure de propionyle (30)	Jaune (33)
37	Idem.....	Acide 2-N-méthylamino-8-naphtol-6-sulfonique (19)	Alcalines (26)	Chlorure de benzoyle (31)	Rouge (34)
38	Idem.....	Acide 6-bêta-hydroxyéthylsulfonyl-2-naphtol-x-sulfonique. (20)	Idem	Anhydride acétique (28)	Rouge (36)
39	o-anisidine.....	Idem.....	Idem	Idem	orangé
40	4 - sulfon - N - (bêta - hydroxyéthyl)amide de l'aniline.	Acide 1-naphtol-4-sulfonique (21)	Idem	Chlorure de butyle (32)	Rouge (36)
41	4 - sulfon - N - (bêta - hydroxyéthyl)amide de l'aniline.	Acide 2-amino-8-naphtol-6-sulfonique. (22)	Acides (27)	Anhydride acétique (28)	Rouge (36)
42	4 - sulfon N : N di (bêta hydroxyéthyl) amide de l'aniline.	Acide 1-naphtol-4-sulfonique. (23)	Alcalines (26)	Idem	Idem
43	4 - bêta - hydroxyéthyl sulfonylaniline.	Idem.....	Idem	Idem	Orangé (35)
44	Idem.....	1 - (3' - sulfophényl) - 3 - méthyl - 5 - pyrazolone.	Idem	Idem	Jaune (33)
45	Idem.....	Acide 2-amino-8-naphtol-6-sulfonique (24)	Acides (27)	Anhydride acétique (28)	Rouge (34)
46 (6)	Acide 4-bêta-hydroxyéthylsulfonylaniline 2 : 6-disulfonique.	1-phényl-3-méthyl-5-pyrazolone....	Alcalines (26)	Idem	Jaune (33)
47	p-nitroaniline.....	Acide 6-bêta-hydroxyéthylsulfonyl-2-naphtol-x-sulfonique. (25)	Idem	Idem	Orangé (35)
48 (7)	Acide 2-naphtylamine-6-sulfonique.	1 - (3' - bêta - hydroxyéthylsulfonyl-phényl)-3-méthyl-5-pyrazolone.	Idem	Idem	Idem
49 (8)	Acide orthanilique.....	2 - naphtylamine - 6 - bêta - hydroxyéthylsulfone.	Acides (27)	Idem	Idem

[Key to previous page:]

Key:	1	Example
	2	Coupler
	3	Coupling conditions
	4	Acyating agent
	5	Shade
	6	4-beta-Hydroxyethylsulfonylaniline 2,6-disulfonic acid
	7	2-Naphthylamine-6-sulfonic acid
	8	Orthanilic acid
	9	1-Naphthol-4-sulfonic acid
	10	2-Naphthol-6-sulfonic acid
	11	2-Naphthol-7-sulfonic acid
	12	1-Naphthol-5-sulfonic acid
	13	2-Amino-5-naphthol-7-sulfonic acid
	14	2-Amino-8-naphthol-6-sulfonic acid
	15	m-Phenylenediaminosulfonic acid
	16	2-N-Methylamino-8-naphthol-6-sulfonic acid
	17	2-N-Acetyl-amino-5-naphthol-7-sulfonic acid
	18	m-Phenylenediaminesulfonic acid
	19	2-N-Methylamino-8-naphthol-6-sulfonic acid
	20	6-beta-Hydroxyethylsulfonyl-2-naphthol-x-sulfonic acid
	21	1-Naphthol-4-sulfonic acid
	22	2-Amino-8-naphthol-6-sulfonic acid
	23	1-Naphthol-4-sulfonic acid
	24	2-Amino-8-naphthol-6-sulfonic acid
	25	6-beta-Hydroxyethylsulfonyl-2-naphthol-x-sulfonic acid
	26	Alkaline
	27	Acidic
	28	Acetic anhydride
	29	Acetyl chloride
	30	Propionyl chloride
	31	Benzoyl chloride
	32	Butyryl chloride
	33	Yellow
	34	Red
	35	Orange
	36	Orange red
	37	Brown

### Example 50

53.1 parts of the copper complex of 2-(2'-hydroxy-5'-beta-hydroxyethylsulfonylphenylazo)-1-naphthol-4-sulfonic acid are stirred in 500 parts pyridine at a temperature of 20°C, and 30 parts acetic anhydride are gradually added with the temperature of the mixture maintained at 20°C by external cooling. The mixture is then stirred for 16 h at 20°C, 1000 parts diethyl ether are added, the precipitated coloring agent is separated by filtration, it is washed with a 10% aqueous sodium chloride solution, and it is dried.

Applied to cellulose textile materials along with a treatment with an acid fixing agent, the coloring agent produces red shades with very good fastness with regard to washing and to light.

The copper complex used in the example above can be obtained by coupling diazotized 2-aminophenol-4-beta-hydroxyethylsulfone with 1-naphthol-4-sulfonic acid in an alkaline medium, and by then heating the resulting azo compound with an aqueous solution of copper acetate.

The following table gives other examples (Nos. 51-59) of new coloring agents of the invention, which are obtained by replacing the 53.1 parts of the copper complex used in Example 50 by equivalent quantities of metallic complexes which are obtained by diazotizing the amine indicated in column 2 of the table, by coupling with the coupler indicated in column 3 of the table and by then treating the resulting azo compound with a metallizing agent providing the metal indicated in column 4 of the table and/or by replacing the 30 parts acetic anhydride used in Example 50 by equivalent quantities of the acylating agents indicated in column 5 of the table. Column 6 of the table indicates the shades obtained when the coloring agents are applied to textile materials.

Exemple (1)	Amine	Copulant (2)	Métal	Agent d'acylation (3)	Tainte (4)
51	2 - aminophénol - 4 - bêta - hydroxyéthylsulfone.	Acide 2-amino-5-naphtol-7-sulfonique. (5)	Cuivre (8)	Anhydride acétique (10)	Rubis (13)
52	Idem.....	Idem.....	Idem	Chlorure de benzoyle (11)	Idem
53	Idem.....	1 - (2' : 5 - dichloro - 4' - sulfophényl) - 3-méthyl-5-pyrazolone.	Idem	Anhydride acétique (10)	Jaune (16)
54	Idem.....	Acide 1-naphtol-4-sulfonique (6)	Idem	Chlorure d'acryloyle (12)	Rouge (14)
55	Idem.....	Acide 2-naphtol-6-sulfonique (7)	Idem	Anhydride acétique (10)	Idem
56	Idem.....	1 - (2' : 5' - dichloro - 4' - sulfophényl) - 3-méthyl-5-pyrazolone.	Chrome (9)	Idem (10)	Orange (15)
57	Idem.....	Idem.....	Cobalt	Idem	Jaune (16)
58	2 - aminophénol - 4 - sulfon - N - éthyl - N - bêta - hydroxyéthylsulfonamide.	1 - (4' - sulfophényl) - 3 - méthyl - 5 - pyrazolone.	Cuivre (8)	Idem	Idem
59	2 - aminophénol - 4 - sulfon - N : N - di(bêta - hydroxyéthyl)sulfonamide.	1 - (2' - chloro - 5' - sulfophényl) - 3 - méthyl-5-pyrazolone.	Idem	Idem	Idem

- Key:
- 1 Example
  - 2 Coupler
  - 3 Acylating agent
  - 4 Shade
  - 5 2-Amino-5-naphthol-7-sulfonic acid
  - 6 1-Naphthol-4-sulfonic acid
  - 7 2-Naphthol-6-sulfonic acid
  - 8 Copper
  - 9 Chromium
  - 10 Acetic anhydride
  - 11 Benzoyl chloride
  - 12 Acryloyl chloride
  - 13 Ruby
  - 14 Red
  - 15 Orange
  - 16 Yellow

#### Example 60

A solution of 28.9 parts 2-methoxy-5-beta-acetoxyethylsulfonylaniline, in a mixture of 25 parts of a concentrated aqueous hydrochloric acid solution and 500 parts water, is cooled to 2°C, and while stirring, a solution of 6.9 parts sodium nitrite in 60 parts water is added. The mixture is stirred for 15 min, the excess nitrous acid is then eliminated by addition of sulfamic acid, and the

mixture is then added to a suspension of 24.5 parts 2-naphthylamine-6-sulfonic acid in 500 parts water. Sodium acetate is then added until the mixture is no longer acidic with Congo Red, and the mixture is then stirred for 16 h at 5°C. The precipitated solid is then separated by filtration, and the solid thus obtained is stirred in 750 parts water, and sodium carbonate is added until the mixture is alkaline. 75 parts sodium chloride are then added, the precipitated coloring agent is separated by filtration, and it is dried.

Applied to cellulose textile materials along with treatment with an acid fixing agent, this coloring agent produces orange shades with very good fastness with regard to wet treatments.

Instead of the 28.9 parts 2-methoxy-5-beta-acetoxyethylsulfonylaniline used in the example above, 27.75 parts 2-chloro-5-beta-acetoxyethylsulfonylaniline are used and/or instead of the 24.5 parts 2-naphthylamine-6-sulfonic acid used in the example above, 26.1 parts 2-amino-8-naphthol-6-sulfonic acid are used, and similar coloring agents are obtained.

#### Example 61

A solution of 1.4 parts sodium nitrite in 10 parts water is added to a solution of 6.6 parts 2-methoxy-5-beta-acetoxyethylsulfonylaniline in a mixture of 100 parts water and 3 parts of a concentrated aqueous hydrochloric acid solution at a temperature of 0°C, and the resulting mixture is stirred for 15 min. Sulfamic acid is then added in order to destroy any excess nitrous acid which is present. The resulting solution is then added to a solution of 8.5 parts 1-amino-8-naphthol-3,6-disulfonic acid in 100 parts water, and the mixture is then kept for 3 h at 5°C. The precipitated monoazo compound is then separated by filtration, the resulting solid is stirred in 200 parts water, and a 2N aqueous sodium hydroxide solution is then added until the mixture is alkaline with Brilliant Yellow. The resulting solution receives the addition of a solution of diazotized 2-methoxy-5-beta-acetoxyethylsulfonylaniline, which is obtained as described in the first phase of this example, and the mixture is stirred for 16 h at 5°C, with addition of sodium carbonate in order to keep the mixture alkaline with Brilliant Yellow. 35 parts sodium chloride are then added, and the precipitated coloring agent is separated by filtration, it is washed with a 5% aqueous sodium chloride solution, and it is dried.

Applied to cellulose textile materials along with a treatment with an acid fixing agent, the coloring agent produces navy blue shades with an excellent fastness with regard to wet treatments.

#### Example 62

A mixture of 27 parts of 3-nitro-4-chlorobenzene-beta-hydroxyethylsulfone, 21.5 parts metanilic acid, 30 parts calcium carbonate, 100 parts ethyl alcohol and 200 parts water are stirred at boiling for 17 h under a reflux condenser, and the mixture is then filtered. The resulting

filtered liquor is cooled to 15°C, the precipitated solid is separated by filtration, it is washed with ethyl alcohol, and it is dried. The resulting solid is dissolved in 300 parts pyridine at a temperature of 20°C, 20 parts acetic anhydride are added, and the mixture is stirred for 17 h at 20°C. The mixture is then distilled under reduced pressure in order to eliminate the pyridine, and the residue is stirred with diethyl ether. The precipitated coloring agent is then separated by filtration, it is washed and dried.

Applied to cellulose textile materials along with treatment with an acid fixing agent, the coloring agent produces yellow shades with very good fastness with regard to wet treatments.

#### Example 63

A mixture of 13 parts 3-nitro-4-chlorobenzenesulfone-N-(beta-hydroxyethyl)amide, 8.5 parts metanilic acid, 13 parts calcium carbonate, 45 parts ethyl alcohol and 100 parts water are stirred at boiling under a reflux condenser for 25 h. The mixture is then filtered, and the resulting filtered liquor is evaporated to dryness. The residual solid is dissolved in 100 parts ethanol, 30 parts potassium acetate are added, the precipitated solid is separated by filtration, and it is dried. The resulting solid is dissolved in 300 parts pyridine, 22 parts acetic anhydride are added, and the mixture is stirred for 5 h at 25°C. At rest, the resulting mixture separates into two layers, the lower layer is separated, and it is added to 500 parts of a light petroleum ether (which boils between 40 and 60°). The resulting solid is then separated by filtration, it is washed with acetone, and ether is added. The precipitated coloring agent is then separated by filtration, and it is dried.

The table above gives other examples (No. 64-70) of new coloring agents of the invention



Exemple (1)	Composé anthraquinonique (2)	Agent d'acylation (3)	Teinte (4)
64	Acide 1-amino-4-(3'-bêta-hydroxyéthylsulfonylanilino) anthraquinone-2-sulfonique. (5)	(10) anhydride propionique	Bleu-rougeâtre (14)
65	<i>Idem</i> ..... (5)	(11) chlorure de benzoyle <i>Idem</i>	<i>Idem</i>
66	Acide 1-amino-4-[4'-méthyl-3'-bêta-hydroxyéthylsulfonylméthyl]anilino]anthraquinone-2-sulfonique. (6)	<i>Idem</i>	Bleu (15)
67	<i>Idem</i> ..... (6)	(12) chlorure d'acétyle	<i>Idem</i>
68	Acide 1-amino-4-(4'-bêta-hydroxyéthylsulfonyl-anilino) anthraquinone-2-sulfonique. (7)	(13) anhydride acétique <i>Idem</i>	Bleu-rougeâtre (14)
69	Acide 1-amino-4-[3'-sulfon-N-bêta-hydroxyéthylamido]anilino]anthraquinone-2-sulfonique. (8)	<i>Idem</i>	<i>Idem</i>
70	Acide 1-amino-4-[3'-(sulfon-N-alpha-éthyl-bêta-hydroxyéthylamido)anilino]anthraquinone-2-sulfonique. (9)	<i>Idem</i>	<i>Idem</i>

- Key:
- 1 Example
  - 2 Anthraquinone compound
  - 3 Acylation agent
  - 4 Shade
  - 5 1-Amino-4-(3'-beta-hydroxyethylsulfonylanilino)anthraquinone-2-sulfonic acid
  - 6 1-Amino-4-(4'-methyl-3'-beta-hydroxyethylsulfonylmethyl)anilinoanthraquinone-2-sulfonic acid
  - 7 1-Amino-4-(4'-beta-hydroxyethylsulfonylanilino)anthraquinone-2-sulfonic acid
  - 8 1-Amino-4-(3'-sulfon-N-beta-hydroxyethylamido)anilino)anthraquinone-2-sulfonic acid
  - 9 1-Amino-4-(3'-(sulfon-N-alpha-ethyl-beta-hydroxyethylamido)anilinoanthraquinone-2-sulfonic acid
  - 10 Propionic anhydride
  - 11 Benzoyl chloride
  - 12 Acetyl chloride
  - 13 Acetic anhydride
  - 14 Reddish blue
  - 15 Blue

which are obtained when the twelve parts of

1-amino-4-(3'-beta-hydroxyethylsulfonylanilino)anthraquinone used in Example 2 are replaced by equivalent quantities of the anthraquinone compounds listed in column 2 of the table and/or the 7.6 parts acetic anhydride used in Example 2 are replaced by equivalent quantities of the

acylating agents listed in column 3 of the table. Column 4 of the table indicates the shades obtained when these coloring agents are applied to textile materials.

#### Example 71

14.4 parts copper phthalocyanine are added to 163 parts chlorosulfonic acid, and the resulting mixture is stirred for 4 h between 135 and 140°C. The mixture is then cooled to 10°C, it is poured into a mixture of water and ice, and the precipitated chlorosulfonated copper phthalocyanine is separated by filtration, and it is washed with water containing ice. The resulting mixture is stirred with 120 parts water and 120 parts ice, and a 10N aqueous sodium hydroxide solution is added until the mixture is neutral using methyl orange [as an indicator]. A solution of 9.1 parts meta-aminobenzene-beta-acetoxyethylsulfone in 100 parts acetone and 16.8 parts sodium bicarbonate is then added, and the resulting mixture is stirred for 24 h at a temperature between 20 and 25°C. 50 parts sodium chloride are then added, and the precipitated coloring agent is separated by filtration and dried.

Applied to cellulose textile materials along with treatment with an acid fixing agent, the coloring agent produces greenish-blue shades with excellent fastness with regard to wet treatments.

Instead of the 9.1 parts meta-aminobenzene-beta-acetoxyethylsulfone used in the preceding example, 11.4 parts meta-aminobenzene-beta-benzoyloxyethylsulfone or 12.5 parts 3-(beta-benzoyloxyethylsulfonylmethyl)-4-methylaniline or 10.2 parts 3-(beta-acetoxyethylsulfonylmethyl)-4-methylaniline are used, and similar coloring agents are obtained.

#### Example 72

14.4 parts copper phthalocyanine are added to 68 parts chlorosulfonic acid, and the resulting mixture is stirred for 3 h at a temperature between 135 and 140°C. The mixture is then cooled to 95°C, 5.9 parts phosphorus trichloride are added [over a period of] two hours, and the mixture is then stirred for two hours at 100°C. The mixture is cooled to 10°C, it is poured into a mixture of water and ice, the precipitated chlorosulfonated copper phthalocyanine is separated by filtration, and it is washed with 125 parts of a 1% aqueous hydrochloric acid solution. The resulting solid is stirred with 125 parts water and 75 parts ice, and 6.1 parts meta-aminobenzene-beta-acetoxyethylsulfone are added. A 2N aqueous ammonium hydroxide solution is then added until the pH of the mixture is equal to 8, and this mixture is then heated to 40°C and maintained at this temperature until there is no longer any need to add the 2N aqueous ammonium hydroxide solution in order to maintain the pH of the mixture at 8. An aqueous hydrochloric acid solution is

then added until the pH of the mixture is equal to 7, 50 parts sodium chloride are added, and the precipitated coloring agent is separated by filtration and dried.

Applied to cellulose textile materials along with treatment with an acid fixing agent, the coloring agent produces greenish-blue shades with excellent fastness with regard to wet treatments.

Instead of the 6.1 parts meta-aminobenzene-beta-acetoxyethylsulfone used in the preceding example, 11.4 parts meta-aminobenzene-beta-benzoyloxyethylsulfone or 10.15 parts 3-(beta-acetoxyethylsulfonylmethyl)-4-methylaniline or 12.5 parts 3-(beta-benzoyloxyethylsulfonylmethyl)-4-methylaniline are used, and similar coloring agents are obtained.

#### Example 73

Instead of the chlorosulfonated copper phthalocyanine used in Example 71, one uses an equivalent quantity of (copper phthalocyanine)tetrasulfonyl chloride which is obtained by the process described in Example 1 of United Kingdom Patent No. 515,637 of June 8, 1938, and similar coloring agents are obtained.

#### Example 74

Instead of the chlorosulfonated copper phthalocyanine used in Example 72, one uses a chlorosulfonated copper phthalocyanine obtained by adding 24.7 parts of the tetrasodium salt of (copper phthalocyanine)-tetra-4-sulfonic acid to 120 parts chlorosulfonic acid, stirring the mixture for three hours at 120°C, cooling to 80°C, adding 12 parts thionyl chloride, stirring the resulting mixture for two hours at 120°C, cooling to 20°C, pouring the mixture into ice and water, and separating the precipitated chlorosulfonated copper phthalocyanine by filtration, and similar coloring agents are obtained.

#### Example 75

20 parts "Botany" woolen serge are immersed in a dyeing fluid consisting of a solution of 0.2 part of the coloring agent of Example 15 and 0.6 part ammonium acetate in 1000 parts water at a temperature of 40°C, the dyeing fluid is then heated to 100°C for 30 min, and it is maintained at 100°C for one hour. The dyed woolen serge is then removed from the dyeing fluid, it is rinsed with water and dried.

The woolen serge is dyed a greenish-yellow shade with good fastness with regard to washing and to light.

#### Example 76

20 parts "Botany" wool tufts are immersed in a dyeing fluid consisting of a solution of 0.2 part of the coloring agent of Example 2, 0.2 part acetic acid and 2 parts sodium sulfate in 1000 parts water at a temperature of 40°C, the dyeing fluid is then heated to 100°C for 30 min, and it is maintained at this temperature for one hour. The dyed wool tuft is then removed from the dyeing fluid, it is rinsed with water and dried.

The wool tuft is dyed a vivid reddish-blue shade which has good fastness with regard to washing and to light.

#### Example 77

100 parts of a bleached mercerized cotton fabric are padded in a solution of 10 parts of the coloring agent of Example 2 and 2 parts of a nonionic wetting agent in 1000 parts water at a temperature of 40°C, and the cotton fabric is then pressed between rollers until its weight is equal to 200 parts. The cotton fabric is dried at 70°C, and the cotton fabric is then run through a solution 10 parts sodium hydroxide and 300 parts sodium chloride in 1000 parts water, the fabric is pressed between rollers, and it is then subjected to steaming for 30 sec at a temperature of 102°C. The dyed cotton fabric is then "soaped" for 5 min in a 0.5% aqueous solution of a synthetic detergent at a temperature of 95°C, the fabric is rinsed with water and dried. The cotton fabric is colored a vivid reddish blue with excellent fastness with regard to light and to wet treatments.

#### Example 78

100 parts of a cotton poplin fabric are padded in a solution of 15 parts of the coloring agent of Example 26, 10 parts sodium bicarbonate and 2 parts of a nonionic wetting agent in 1000 parts water at a temperature of 20°C, and the cotton fabric is then pressed between rollers until its weight is equal to 200 parts. The cotton fabric is dried at 70°C, and it is then subjected to steaming for one minute at 102°C. The cotton fabric is then "soaped" for one minute in a 0.5% aqueous solution of a nonionic detergent at a temperature of 95°C, the fabric is rinsed in water and finally dried. The cotton fabric is dyed an orange color with excellent fastness with regard to light and to wet treatments.

#### Example 79

5 parts of bleached cotton yarn are immersed in a dyeing fluid consisting of a solution of 0.1 part of the coloring agent of Example 51 and 4.5 parts sodium chloride in 150 parts of water at a temperature of 60°C, and the dyeing is carried out for 30 min at this temperature. 0.3 part sodium hydroxide is then added, and the dyeing is continued for another hour at the same

temperature. The dyed cotton yarn is then removed from the dyeing fluid, this yarn is immersed for 5 min in an 0.3% aqueous solution of a nonionic detergent at a temperature of 100°C, it is rinsed in water and finally dried. The cotton yarn is dyed a ruby color which has excellent fastness with regard to light and to wet treatments.

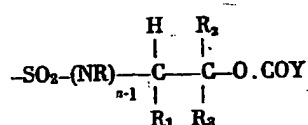
### Example 80

100 parts of a plain-weave cotton fabric are immersed in a solution of 5 parts of the coloring agent of Example 16, 10 parts sodium bicarbonate, 200 parts urea and 2 parts of a nonionic wetting agent in 1000 parts water at a temperature of 25°C, and the cotton fabric is then pressed between rollers until its weight is equal to 200 parts. The cotton fabric is then cooked for 5 min at a temperature of 120°C. The colored cotton fabric is then immersed for 1 min in a 0.5% aqueous solution of a nonionic detergent at a temperature of 95°C, the fabric is rinsed in water and finally dried. The cotton fabric is colored yellow with an excellent fastness with regard to light and to wet treatments.

### Summary

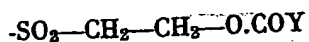
A. As new industrial products: new water-soluble coloring sulfones, characterized by the following points considered alone or in combinations:

1. These coloring agents contain at least one sulfonic acid group or carboxylic acid group, and they contain, attached to a carbon atom of the coloring agent, a group corresponding to formula:



in which R represents a hydrogen atom or an alkyl, substituted alkyl, aryl or substituted aryl group, a cycloalkyl or aralkyl radical; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can represent, independently from one another, hydrogen or lower alkyl groups; "n" has a value of 1 or 2, and -CO.Y represents the radical of a carboxylic monoacid.

2. These coloring agents contain at least one sulfonic acid or carboxylic acid group, and they contain one or two groups with formula:

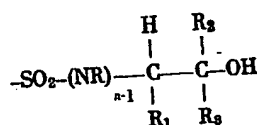


in which Y has the meaning defined under 1;

3. Y represents a lower alkyl radical or a monocyclic aryl radical.

B. A process for the manufacturing of the new coloring sulfones as defined under A, characterized by the following points considered alone or in combinations:

4. A coloring agent which contains at least one sulfonic acid group or carboxylic acid group and which contains, attached to a carbon atom of this coloring agent, a group corresponding to formula:



is treated with a carboxylic monoacid with formula: Y.COOH or with the anhydride or the halide of this acid, the symbols R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, Y and "n" having the meaning defined under 1;

5. The treated coloring agent contains one or two groups: -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH;

6. Coloring agent intermediates which contain at least one group corresponding to the formula defined under 1 and containing at least one carboxylic acid or sulfonic acid group are reacted together;

7. In order to manufacture new water-soluble azo coloring agents which are in accordance with the definition given under 1, a primary aromatic amine is diazotized, and the diazo compound thus obtained is coupled with a coupler, the primary aromatic amine or the coupler or the two containing at least one of the groups whose formula was defined under 1, and the primary aromatic amine or the coupler or the two containing at least one sulfonic acid or carboxylic acid group.

C. A process for coloring cellulose textile material, characterized by the following points considered alone or in combination:

8. The cellulose textile material is treated with a new coloring sulfone as defined under A;

9. The treatment with the coloring agent is carried out along with treatment with an acid fixing agent.